Sandia National Laboratories May/June 2003 Volume 25, No. 3

Combustion Research Facility NEWS

The Origin of Prompt CO_2 Discovered

In the 1970s, combustion scientists in Germany observed that lean acetylene flames produce CO_2 very early in the combustion process. Although it was well known that the reaction $OH + CO \rightarrow H + CO_2$ causes CO_2 to appear much later in the combustion process, the origin of the "prompt" CO_2 remained a mystery until the recent work of Sandians Stephen Klippenstein, Jim Miller, and David Osborn.

Klippenstein and Miller recently proposed a new mechanism to explain prompt CO_2 formation:

$$O + C_2H_2 \rightarrow HCCO + H \qquad (1)$$

$$HCCO + O_2 \rightarrow H + CO + CO_2 \qquad (2a)$$
$$\rightarrow OH + CO + CO \qquad (2b).$$

The reaction of a radical (O or HCCO) with a stable molecule makes this explanation attractive. The high concentration of the stable molecule might explain why the CO_2 is created just as rapidly as the partially oxidized CO molecule at early positions in the flame.

Klippenstein and Miller performed electronic structure calculations that mapped the energy landscape of the reactions. With this information, they predicted the product branching ratios using sophisticated direct dynamics trajectory calculations and master equation simulations. They found that ~90% of the HCCO intermediate in reaction (2) produces $H + CO + CO_2$. Unfortunately the only experimental measurements were indirect, and suggested that the products were $OH + CO + CO$.

To provide direct experimental measurements for the reaction products, Osborn probed the $HCCO + O_2$ reaction using time-resolved fourier transform emission spectroscopy (TF-FTES). In this experiment, the photodissociation of ethyl ethynyl ether ($HCCOC_2H_5$) produces the HCCO intermediate within 20 ns. Using TR-FTES, Osborn was able to observe the reactant, HCCO, and all the possible molecular products (CO, CO_2, and OH) simultaneously.

The 200 sequential time-resolved infrared spectra, shown in Figure 1, document the chemical progress from reactants to products. At the earliest time, strong emission from HCCO is observed in the asymmetric stretching band from 1800 to 2100 cm^{-1}. The HCCO radical is rapidly cooled, and its emission correspondingly decays due to vibrational energy transfer through molecular collisions. Figure 1 clearly shows the rise of CO and CO_2 products with significant vibrational excitation due to the large amount of energy released by reaction (2). Osborn found no evidence for the OH product of channel (2b), and placed an upper limit of < 10% for the contribution of the OH + CO + CO channel.

The single spectrum at the top of Figure 1, taken 490 µs after reaction initiation, clearly identifies the products from their rotationally resolved spectra. Furthermore, the dynamics of the reaction are manifested in the product vibrational state distributions provided by this spectrum, which shows excitation in the CO molecule of up to 11 vibrational quanta. These experiments are consistent with a four-centered reaction intermediate predicted by Klippenstein and Miller, and provide experimental confirmation of their theoretical results.

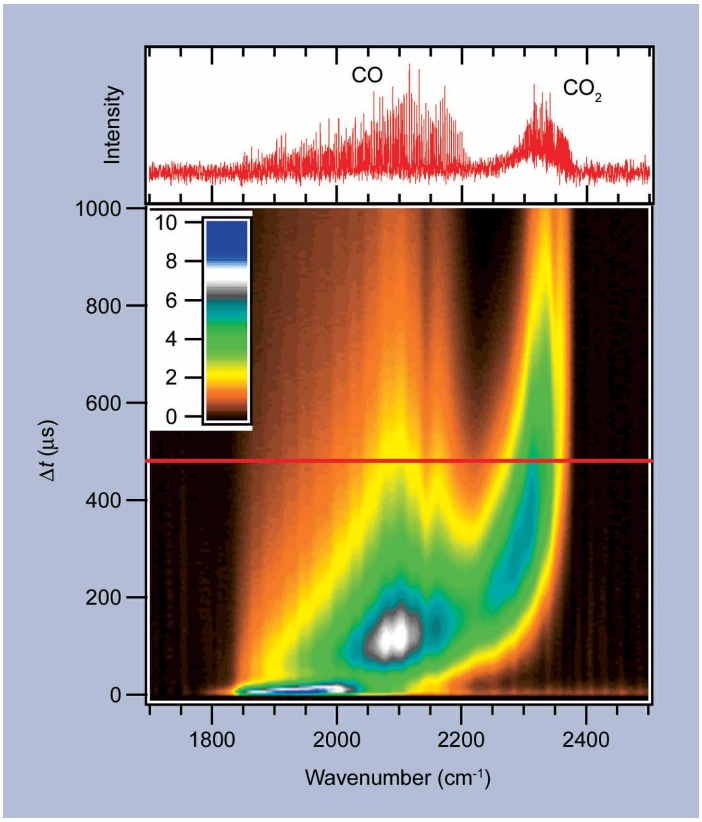

Figure 1. Time-resolved fourier emission spectra of the HCCO + O_2 reaction. The image comprises 200 spectra, each separated by 5 µs. The horizontal red bar gives the measurement time of the high-resolution spectrum at the top of the figure.

One-Dimesional Turbulence Model used to Study Type Ia Supernovae

CRF researchers Alan Kerstein and Scott Wunsch have teamed with Stan Woosley's astrophysics group at UC Santa Cruz (funded by Scientific Discovery through Advanced Computing) and members of the Accelerated Strategic Computing Initiative (ASCI) Alliance Center at the University of Chicago to study thermonuclear combustion in stars. Recently, the team has focused on Type Ia supernovae, a class of violent stellar explosions in which an entire star is vaporized. The massive energy released by these explosions makes them visible from distant galaxies. For this reason, astronomers use Type Ia supernovae as "measuring sticks" to chart the expansion of the universe. Many questions about the mechanics of the Ia supernovae remain unanswered. Alan and Scott's team is working to answer some of these questions.

The stellar precursors of the Ia supernovae are white dwarfs–remnants left behind after stars like our sun have spent their hydrogen fuel. They are composed of very dense (10^9 g/cm^3) ionized carbon and oxygen. The electrons are Fermi degenerate, so the star's fluid properties are similar to those of liquid metals. At the center, where the temperature is highest, the carbon and oxygen fuse to form heavier elements. The energy released heats the fluid, and the resulting buoyancy carries it out of the core before any significant fraction of the nuclei can fuse. Cooler fluid flows in to replace it, resulting in a convective flow that resembles a giant re-circulating engine. During this convecting phase, which may last for millenia, the combustion process in the core is analogous to a distributed reaction zone.

As the core temperature slowly rises, the reaction rate increases rapidly due to the strong temperature sensitivity (approximately T^{23}) in the thermonuclear reaction network. Eventually, a few "sparks" become so hot that their chemical timescales shorten to the point where "flames" are born. Only the hottest points become flames, so it is important to understand the temperature variations that result from the convective mixing in the white dwarf.

Since the large Reynolds number puts the problem far beyond the capabilities of traditional numerical simulation, the group has employed the CRF-developed One-Dimensional Turbulence (ODT) model to study the temperature fluctuations. The model simulations estimate precisely when and where ignition may occur. After ignition, the resulting flames are self-sustaining thermonuclear reaction zones, which propagate through the premixed carbon and oxygen fuel consuming much of the mass of the star and blowing it apart in spectacular fashion. The number and location of the initial ignition points as well as the subsequent flame physics determine the chemical composition of the reaction products.

Although the flame fronts are similar to chemical flames, there are several important differences, such as the "metallic" fluid properties and the very strong turbulence in the Ia flame fronts. The group is performing theoretical and numerical studies to clarify flame behavior in this regime.

The extremely strong turbulence in Ia supernovae make resolved numerical calculations utterly impossible. To date, simulations using simple models for the unresolved ignition conditions and flame propagation have not replicated the observed chemical makeup of explosion products; current understanding of the combustion physics is inadequate. The team's work on ignition and flame propagation will lead to improved modeling and ultimately to more accurate calculations of the complete explosion process. This in turn should increase the Ia's usefulness as an intergalactic measurement tool.

The CRF News is published bimonthly by the Combustion Research Facility, Sandia National Laboratories, Livermore, California, 94551-0969.

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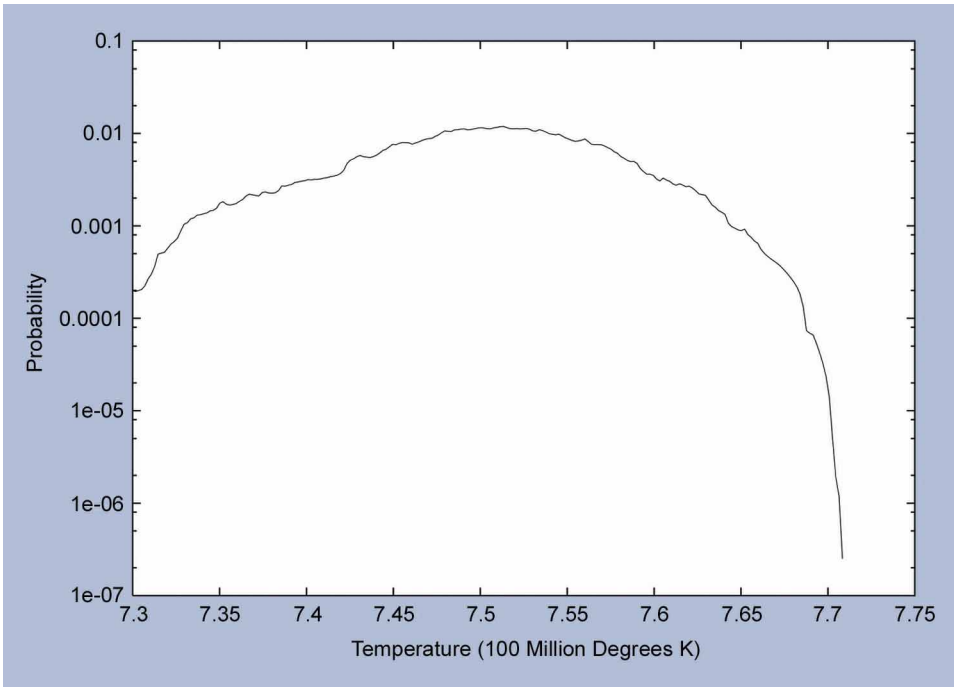

Figure 1. Results of a preliminary ODT calculation of the probabilities of temperature fluctuations during the convective phase of the Ia evolution, when the average temperature is 750 million degrees Kelvin. Flame ignition will occur when the hottest fluctuations reach approximately 800 million degrees Kelvin.

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People

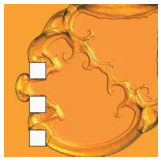
Professor James Valentini of Columbia University visited the CRF for two weeks in March to work with Dave Chandler and Michael Elioff performing crossed-molecular beam, ion-imaging experiments. While at Sandia, Valentini collaborated on a project quantifying the velocity distributions obtained from inelastic collisions between an Ar atom and an NO molecule. From left to right: Michael Elioff, Dave Chandler, James Valentini, and Mark Jaska.

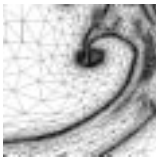
Chris Kennedy, who left the CRF in April 2003, worked with Jackie Chen on the development of high-order finite difference methods for direct numerical simulations. To integrate the governing species continuity and energy equations with stiff chemical source terms, Chris has developed a new high-order additive Runge-Kutta method for coupling stiff source terms with non-stiff transport terms. Chris also worked closely with Habib Najm and Jaideep Ray to develop high-order differencing and interpolation stencils for adaptive mesh refinement.

John DeSain, a postdoctoral associate and limited term employee in the Combustion Chemistry department since 1999, has taken a position as a member of the technical staff in the Propulsion Science and Experimental Mechanics Department at the Aerospace Corporation. At Sandia, John worked with Craig Taatjes, using infrared spectroscopy to investigate elementary reaction kinetics of combustion systems, notably measuring product formation in reactions of alkyl radical with molecular oxygen.

Clarification

The two meshing images that appeared in the March/April CRF News were created by Jean-François Remacle (Université Catholique de Louvain, Belgium). Look for further information on meshing and more examples of Remacle's work in the July/August CRF News.





Sandians Present Papers at the SAE World Congress

The Society of Automotive Engineers (SAE) World Congress is the premier meeting worldwide dedicated to mobility engineering. It was held in Detroit, Michigan on March 3-6 this year. John Dec, Paul Miles, and Mark Musculus represented the CRF Engine Combustion program by presenting papers on homogeneous charge, compression ignition (HCCI), swirl-supported diesel, and heavy-duty diesel combustion processes (respectively). A major focus of the meeting this year was on low-temperature, compression-ignition combustion processes, which offer the potential for ultra-low, engine-out emissions.

BES Peer Review

The 2003 BES peer review took place March 31- April 2. Each spring, external peers visit the CRF to review our DOE/BES-supported Combustion Sciences Research Program. Members of this year's review panel were (from left to right) Graham Glass (Rice University), Jack Howard (MIT), Bill Kirchhoff (DOE), Eric Rohlfing (DOE), Jüergen Troe (Universität Göttingen, Germany), and Thanh Truong (University of Utah).

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under contract DE-AC04-94AL85000

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